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Solid state synthesis, processing, and electrical properties of $Sr(Ti_xZr_{1-x})O_3$ ($0 \le x \le 1$) ceramics for high voltage applications

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Compositions of $Sr(Ti_xZr_{1-x})O_3$ ($0 \le x \le 1$) were prepared by solid state synthesis using the $SrTiO_3$ and $SrZrO_3$ end members obtained from the Pechini method. For the two compositions $Sr(Ti_{0.2}Zr_{0.8})O_3$ and $Sr(Ti_{0.8}Zr_{0.2})O_3$, powder processing routes using 2-propanol as a carrier fluid were developed to prepare tape-cast substrates. The sintering cycles were optimized to obtain specimens that were approximately 99% dense. The relative permittivity, dissipation factor, conductivity, and breakdown strength of $Sr(Ti_xZr_{1-x})O_3$ monolithic capacitors were measured and compared with those of $SrTiO_3$ and $SrZrO_3$. In addition, during breakdown testing, the leakage current as a function of applied voltage was measured.

Key words: $Sr(Ti_xZr_{1,x})O_3$, $SrTiO_3$, $SrZrO_3$, powder processing, dielectric constant, dissipation factor, conductivity, leakage current, breakdown strength.

Introduction

Compositions of $Sr(Ti_xZr_{1-x})O_3$ ($0 \le x \le 1$) are used in a number of applications such as capacitors for integrated circuits, as electroluminescent displays [1], and as microwave dielectrics [2]. For example, $Sr(Ti_{0.8}Zr_{0.2})O_3$ is a widely used substrate that has a moderate dielectric constant of 100-140. The $Sr(Ti_{0.05}Zr_{0.95})O_3$ composition has been demonstrated to be a suitable dielectric at microwave frequencies [3]. When doped, these mixed oxide materials find application as inductance-capacitance filters [4] and as multilayer capacitors [3].

The pure oxide end members SrZrO₃ and SrTiO₃ are also employed in a variety of ways. Strontium zirconate is used for superlattices [5], and doped SrZrO₃ is a proton conductor for solid oxide fuel cells [6]. Strontium titanate finds application as a substrate for superconductors [7], as photoelectrodes [8], and as a capacitor material [9-13].

In addition to this widespread versatility, compositions of $Sr(Ti_xZr_{1-x})O_3$, including the end members, have also been reported to have high breakdown strength [1, 11-14], primarily in thin film applications, but also as monolithic devices. The high breakdown strength of these compositions may arise for a number of reasons. Because neither orthorhombic $SrZrO_3$ nor cubic $SrTiO_3$ is ferroelectric, these materials will not experience electromechanical coupling, which may exacerbate dielectric breakdown. Over the composition range of x=0.4-0.95, the crystal symmetry is tetragonal [15]; these compositions have not been reported to be ferroelectric either. An additional advantage of these materials is that both the Sr and Zr cations exist in single, highly stable, valence states; Ti, however, is known to exist in several valence states. Another potential advantage in this system is that none of the cations Sr, Zr, and Ti volatilizes appreciably at high temperature during sintering, and this may facilitate preparing highly crystalline, phase-pure materials.

The synthesis of $Sr(Ti_xZr_{1-x})O_3$ compositions have been accomplished by a variety of methods including the Pechini method [3, 16], the sol-gel method [1, 17], and by solid state synthesis using a mixture of SrCO₃, ZrO₂, and TiO₂ [14, 15]. Among these synthesis methods, the routes starting from liquid-phase precursors afford several advantages such as atomic level mixing and phase purity. If nominally phase-pure SrZrO₃ and SrTiO₃ can be obtained by liquid-phase syntheses, this may be advantageous in preparing phase-pure intermediate compositions.

In this work, we prepare four compositions, $SrZrO_3$, $Sr(Ti_{0.2}Zr_{0.8})O_3$, $Sr(Ti_{0.8}Zr_{0.2})O_3$, and $SrTiO_3$, in the solid solution system and systematically investigate their processing and electrical properties for high-voltage application as monolithic capacitors. Of the four materials, the two zirconium-rich compositions are orthorhombic, $Sr(Ti_{0.8}Zr_{0.2})O_3$ is tetragonal, and $SrTiO_3$ is cubic. To prepare these compositions, we have synthesized the pure end members by the Pechini method. Earlier work by us has shown that the end members can be processed into dense substrates with breakdown strengths of 35-40 V/µm [12]. In order to be able to prepare any composition in the $SrZrO_3$ -SrTiO_3 solid solution system,

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we use powders of the pure end members and prepare substrates of the mixed oxide compositions by a combined solid-state reaction and sintering method.

Because we are interested in preparing dielectric materials with high breakdown strength, various powder processing conditions have been examined in order to obtain high solids loading in the slurries used to prepare the tape-cast substrates. Earlier work by us has shown that for the end member compositions, high green density translates to higher density in the sintered state [11, 12]. In addition, we have found the optimum sintering temperature, as indicated by sintered density, for each composition. Finally, the electrical properties of dielectric constant, dissipation factor, conductivity, and breakdown strength have been measured. During breakdown testing, the leakage current was also monitored, which may be important for the long-term stability of these materials.

Experimental Procedure

The SrZrO₃ and SrTiO₃ powders were synthesized by the Pechini method with the following reagent grade chemicals: zirconium acetate (Zr(CH₃CO₂)₄), strontium nitrate (Sr(NO₃)₂), citric acid (C₆H₈O₇), ethylene glycol (C₂H₅OOH), and 2-propanol, all obtained from Sigma Aldrich Fine Chemical (Milwaukee, WI). The titanium precursor, titanium acetyl acetonate (Tyzor GBA/GBO), was obtained from Dupont (Wilmington, DE).

Because the detailed synthesis methods for SrTiO₃ and SrZrO₃ have been reported elsewhere [12], only a brief summary is given here. To synthesize SrTiO₃, 27.53 g of titanium acetyl acetonate was added to 100 ml (0.1153 g/ml) of strontium nitrate solution over 15 minutes. To this solution, citric acid (0.09 g/ml) and ethylene glycol (18.6 ml) were added, and the mixture was then heated until a glassy transparent resinous mass was formed. The solid mass was then calcined in air at 900°C for 8 h. For the synthesis of SrZrO₃, controlled addition of 0.1275 g/ml strontium nitrate solution was made into a zirconium acetate solution (0.051 g/ml) at 35-40°C. A citric acid solution (0.08 g/ ml) was next added and the mixture was heated to 80-90°C. Following this, ethylene glycol was added and the mixture was further heated until a glassy mass was formed. This resinous mass was finally calcined at 1200°C for 8 h. The XRD patterns (see Figure 1) indicated that phase-pure materials had been synthesized.

To prepare the mixed oxide compositions of $Sr(Ti_{0.2}-Zr_{0.8})O_3$ and $Sr(Ti_{0.8}Zr_{0.2})O_3$, the $SrZrO_3$ and $SrTiO_3$ powders prepared above were mixed in the desired ratios for 48 h in 2-propanol in polyethylene containers using alumina milling media. Slurries were then tape cast and initially dried in a saturated atmosphere of 2-propanol for 2-3 h followed by drying at 95-105°C for 16 h.

The tape cast substrates were then cut into cylindrical

bodies of approximately 18.5 mm diameter. The monolithic substrates of the nominal $Sr(Ti_{0.2}Zr_{0.8})O_3$ and $Sr(Ti_{0.8}Zr_{0.2})O_3$ compositions were then reacted and sintered in air in a single heating cycle on zirconia setters. The cycle used was conducted with a ramp rate of 4 K minute⁻¹ from room temperature to 700°C, a ramp of 5 K minute⁻¹ to the soak temperature for a 1 h hold, and then controlled cooling at a rate of 5 K minute⁻¹ to room temperature. The density of the sintered substrates was determined by measuring the sample weight, dimensions, and by the Archimedes technique; the density of the green substrates was determined from the former method only. Relative densities of the mixed compositions were determined from reported lattice parameters for the orthorhombic and tetragonal compositions [15]. The x-ray diffraction patterns were obtained with CuK_{α} radiation with background subtraction of the sample holder.

For electrical testing, the sintered monolithic substrates were electroded by gold sputtering (~10 nm on each side). The breakdown testing was conducted in a fluorocarbon-based fluid to prevent arcing. During the high-voltage testing, the total current flowing through a substrate connected in series to a 0.5 M Ω resistor was also measured.

Results and Discussion

The powder x-ray diffraction patterns of the Sr(Ti_{0.2}-Zr_{0.8})O₃ and Sr(Ti_{0.8}Zr_{0.2})O₃ materials are shown in Figure 1, along with the patterns of the pure SrZrO₃ and SrTiO₃ end members used to synthesize the mixed oxides. The XRD pattern of the Sr(Ti_{0.2}Zr_{0.8})O₃ composition indicates that it is nominally phase pure and corresponds closely to the orthorhombic pattern of SrZrO₃. Small reflections at 20=32.9 and 36.3° most likely indicate the presence of small amounts of the cubic SrTiO₃ phase. The diffraction pattern of Sr(Ti_{0.2}-Zr_{0.8})O₃ synthesized here is consistent with the patterns reported for the same composition prepared by other



Fig. 1. X-ray diffraction patterns for $SrZrO_3$, $Sr(Ti_{0.2}Zr_{0.8})O_3$, $Sr(Ti_{0.8}Zr_{0.2})O_3$, and $SrTiO_3$.



Fig. 2. Relative green density (left-hand axis) as a function of solids loading in the slurry, and relative sintered density (right-hand axis) as a function of the sintering temperature for $Sr(Ti_{0.2}Zr_{0.8})O_3$ tape cast substrates.

methods [3, 14, 15, 18]. The XRD pattern of the $Sr(Ti_{0.8}Zr_{0.2})O_3$ material in Figure 1 also shows that it is nominally phase pure and is consistent with the diffraction patterns observed for $Sr(Ti_xZr_{1-x})O_3$ compositions for x=0.4-0.95 [15, 18].

The effect of solids loading in the slurry on the green density of $Sr(Ti_{0.2}Zr_{0.8})O_3$ samples is shown in Figure 2. With increasing volume% solids, the green density increases until 67% relative density is achieved at 64 volume%. The absence of overlap of the 95% confidence intervals indicates that this is a statistically significant trend. Figure 2 also indicates that the sintered density of the $Sr(Ti_{0.2}Zr_{0.8})O_3$ composition is sensitive to the hold temperature in the sintering cycle. As the sintering temperature is increased from 1430 to 1470°C, the relative density increases from 92% to >99%; no further increase in the final density was observed for higher sintering temperatures.

Figure 3 shows the same trends for density of the $Sr(Ti_{0.8}Zr_{0.2})O_3$ composition as was observed in Figure 2 for the $Sr(Ti_{0.2}Zr_{0.8})O_3$ composition. Both lower green density and sintered density are obtained for the $Sr(Ti_{0.8}Zr_{0.2})O_3$ material as compared to the *x*=0.2 material. The maximum in the sintered density occurs at a lower temperature for $Sr(Ti_{0.8}Zr_{0.2})O_3$ as compared to $Sr(Ti_{0.2}Zr_{0.8})O_3$. Based on these sintering results, along with the maxima in sintered densities of 1400°C and 1520°C for pure $SrTiO_3$ and $SrZrO_3$ [12], respectively, we see a gradual increase in temperature for the maxima in sintered to the zirconium content of the compositions.

The microstructures for the $Sr(Ti_{0.2}Zr_{0.8})O_3$ and $Sr(Ti_{0.8}Zr_{0.2})O_3$ compositions sintered for 1 h at 1470° and 1440°C, respectively, are shown in Figure 4. For



Fig. 3. Relative green density (left-hand axis) as a function of solids loading in the slurry, and relative sintered density (right-hand axis) as a function of sintering temperature for $Sr(Ti_{0.8}Zr_{0.2})O_3$ tape cast substrates.



Fig. 4. Field-emission micrographs of the as-cast surfaces of $Sr(Ti_{0.2}Zr_{0.8})O_3$ (top panel) and $Sr(Ti_{0.8}Zr_{0.2})O_3$ (bottom panel). The substrates were sintered at 1470° and 1440°C, respectively, for 1 h.

the $Sr(Ti_{0.2}Zr_{0.8})O_3$ material, the average grain size is of the order of 5 µm and the grains typically have 5-7



Fig. 5. (a) Dielectric constant and (b) dissipation factor as a function of frequency for $SrZrO_3$, $Sr(Ti_{0.2}Zr_{0.8})O_3$, $Sr(Ti_{0.8}Zr_{0.2})O_3$, and $SrTiO_3$.

sides per grain. Although all of the sides are not equal, the curvature of the grain boundaries are close to zero, which indicates that a driving force for further grain growth from curvature effects is low. For the $Sr(Ti_{0.8}-Zr_{0.2})O_3$ composition, which was sintered at a lower temperature, slightly smaller grains and some intergranular porosity are evident. The grain size, grain shape, and density of the two mixed-oxide compositions shown here are similar to what has been reported for the pure $SrZrO_3$ and $SrTiO_3$ end members [12, 13].

The dielectric constant for the $Sr(Ti_{0.2}Zr_{0.8})O_3$ and $Sr(Ti_{0.8}Zr_{0.2})O_3$ compositions measured as a function of frequency are displayed in Figure 5a along with the values for the pure $SrZrO_3$ and $SrTiO_3$ end members. The dielectric constants for the $SrZrO_3$, $Sr(Ti_{0.2}Zr_{0.8})O_3$, and $Sr(Ti_{0.8}Zr_{0.2})O_3$ substrates are approximately 60, 85, and 320, respectively, and are nearly constant over the frequency range of 10^2 - 10^5 Hz. The dielectric constant for SrTiO₃, however, decreases from 400 to 180 with increasing frequency, which is consistent with the previously reported data for this material [12, 19].

The dissipation factor as a function of frequency for the same four compositions is shown in Figure 5b; the dissipation factors all decrease with increasing frequency over the range of frequency corresponding to an ion jump mechanism. With the exception of the low frequency data, the loss factors do not show much dependence on composition.

The conductivity as a function of frequency for the



Fig. 6. (a) Conductivity as a function of frequency and (b) leakage current as a function of applied field for $SrZrO_3$, $Sr(Ti_{0.2}Zr_{0.8})O_3$, $Sr(Ti_{0.8}Zr_{0.2})O_3$, and $SrTiO_3$.

four compositions is displayed in Figure 6a. For all of the materials, the conductivity increases with increasing frequency. From Figure 6a, we can also observe that $SrZrO_3$ is the least conductive whereas $SrTiO_3$ is the most conductive; the mixed oxides $Sr(Ti_{0.2}Zr_{0.8})O_3$ and $Sr(Ti_{0.8}Zr_{0.2})O_3$ are intermediate in conductivity. We thus see that increasing the Ti content of the materials leads to an increase in conductivity, especially at frequencies greater than 1000 Hz.

The average breakdown strengths and standard deviations for capacitors of the different compositions are reported in Table 1. For the SrZrO₃ and SrTiO₃ substrates, the average breakdown strengths are in the range of 40-35 V/µm with standard deviations of 14-9.5 V/µm. Individual values as high as 57 and 42 V/ μ m were obtained for the SrZrO₃ and SrTiO₃ materials. For the Sr(Ti_{0.2}Zr_{0.8})O₃ samples, the breakdown strength was found to be 36 V/ μ m, which is close to the breakdown strength of SrTiO₃. Among all the compositions, Sr (Ti_{0.8}Zr_{0.2})O₃ was found to have the lowest breakdown strength of 22 V/µm along with the lowest standard deviation of 2.5 V/um. Individual values of the breakdown strength as high as 43 and 26 V/ μ m were obtained for Sr(Ti_{0.2}Zr_{0.8})O₃ and Sr(Ti_{0.8}Zr_{0.2})O₃, respectively. Because the energy density of a capacitor depends on both the applied voltage and the dielectric constant, the different compositions have different energy densities, as indicated in Table 1. Of the compositions examined

Material	Average thickness (µm)	K @ 1000 Hz -	Breakdown Strength (V/µm)		Energy Density*
			Average	Standard deviation	(J/cm ³)
SrZrO ₃	160	60	40	14.0	0.42
SrTiO ₃	120	380	35	9.6	2.0
Sr(Ti _{0.2} Zr _{0.8})O ₃	152	85	36	6.1	0.49
Sr(Ti _{0.8} Zr _{0.2})O ₃	132	320	22	2.5	0.68

Table 1. Dielectric constant, breakdown strength, and energy density of tape cast substrates sintered at the optimum temperature for 1 hour

*at breakdown field strength

here, $SrTiO_3$ has the highest energy density; the other three compositions have a lower energy density by a factor of 3-5.

During breakdown testing, the total current flow through the capacitor and resistor was monitored. The leakage current as a function of the applied field is shown in Figure 6b for the four compositions. Above 25 V/ μ m, the SrTiO₃ substrates begin to leak current, whereas the leakage current through the other materials is below the detection limit of the measuring device. The larger leakage current of the SrTiO₃ material is consistent with the conductivity data in Figure 6a.

In general, compared to monolithic capacitors of other compositions, all the materials prepared in this work exhibit high-voltage breakdown behavior. We attribute this mainly to the high final densities obtained, which can be attributed to careful powder processing and sintering optimization. We note especially that the material with the lowest relative density also exhibited the lowest breakdown voltage. In addition to processing defects, other factors may contribute to low breakdown behavior, including space charge effects, electromechanical coupling, ohmic heating, and reaction. For the materials prepared here, which are paraelectric, no electromechanical failure mechanism should be operative. Although we cannot definitely conclude which mechanisms are controlling for the breakdown behavior, the presence of zirconium in the compositions does lead to lower AC conductivity and to lower leakage current, which should minimize ohmic heating.

Conclusions

Nominally phase-pure compositions of $Sr(Ti_{0.2}Zr_{0.8})O_3$ and $Sr(Ti_{0.8}Zr_{0.2})O_3$ have been achieved via solid state synthesis by using the previously synthesized $SrTiO_3$ and $SrZrO_3$ end members. Powder processing in 2propanol yielded high solids loading and therefore green densities of about 65% of theoretical. The maximum density of each material was sensitive to the sintering temperature. The dielectric constants of the compositions containing zirconium were independent of frequency, whereas the dielectric constant of $SrTiO_3$ decreased by a factor of two over the frequency range of 10^2-10^5 Hz. The materials $SrZrO_3$, $Sr(Ti_{0.2}Zr_{0.8})O_3$, and $SrTiO_3$ all have breakdown strengths of greater than 35 V/µm, which make them suitable for high-voltage applications. The $SrTiO_3$ composition, however, exhibited the largest AC conductivity and largest leakage current, which may degrade its long-term stability at high voltage.

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